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Side-Chain Sulfonated Poly(arylene ether)s for Fuel Cell Applications

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Summary: Poly(arylene ether sulfone)s of high molecular weight and narrow molecular weight distribution were obtained by melt polycondensation of 4,4′-difluorodiphenylsulfone and trimethylsilylethers of 4,4′-dihydroxydiphenylsulfone and phenylhydroquinone using CsF as catalyst. Although a block-like structure of the polymers could be expected from the course of reaction, only a single T_g ranging from 190 °C to 230 °C could be detected by DSC and which depended on the copolymer composition. Contrary to the sulfonation of similar poly(ether ether ketone)s the poly(arylene ether sulfone)s here reported were sulfonated both in the side chain and the main chain. Nonetheless the sulfonated poly(arylene ether sulfone)s showed high hydrolytic stability in water at 130 °C.

Keywords: fuel cell; poly(arylene ether); sulfonation

Introduction

Fuel cells have gained increasing interest in the past decade due to regulatory pressure to reduce air pollution and the expected shortage of fossile fuels. Among the various types of fuel cells, low-temperature fuel cells such as polymer electrolyte fuel cells (PEFC) or direct methanol fuel cells (DMFC) are best suitable for automotive or mobile applications. Besides the catalysts, the polymer electrolyte membrane plays an important role in such fuel cells. Standard membrane materials for low-temperature fuel cells are still poly(perfluoroalkylsulfonic acid)s like Nafion®. Major drawbacks of these materials, which hinder the introduction of fuel cell technology to the massmarket, are their insufficient performance at temperatures above 100 °C and their high price. These disadvantages have initiated world-wide research activities on the development of new membrane materials for PEMFC.

In general fully aromatic polymers bearing acidic groups and in particular sulfonated poly(arylene ether)s such as poly(arylene ether sulfone)s or poly(arylene ether ketone)s are considered as the most promising candidates for future ion-exchange membranes in fuel cells. Other materials under investigations are for example sulfonated polyimides,[1,2] poly (oxadiazole)s,[3] poly(phthalazinone)s[4,5] or poly(benzimidazole)s.[6,7]

The sulfonated materials are obtained either by sulfonation of the polymer with concentrated sulfuric acid or chlorosulfonic acid or by the use of already sulfonated monomers.[8,9] Although the former method is easy to carry out, it bears some risks and disadvantages. These are mainly degradation of the polymer backbone[10] and the inhomogeneous and uncontrolled distribution of the sulfonic acid groups along the polymer chain. Furthermore the sulfonation occurs at the acitivated sites. Since the sulfonation of aromatic rings is reversible these sites are most sensitive to hydrolytic cleavage of the sulfonic acid group.

Recently Vogel et al. reported on the unexpected high hydrolytic stability of

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Table 1.
Properties of silylated bisphenols.

Silylated Bisphenol	Yield (%)	b.p. °C (mbar)	Literature
4,4′-dihydroxydiphenylsulfone	99	230–240[a)] ($6–9 \times 10^{-3}$) m.p. 89	m.p. 90 °C[17]
2,5-dihydroxybiphenyl	99	118 (6.5×10^{-2})	

a) Distillation via short-pass distillation equipment; oil bath temperature.

polystyrene sulfonic acid in water at high temperatures up to 200 °C.[11]

These results led us to the idea to prepare chemically stable poly(arylene ethers) with a pending phenyl ring in order to mimic poly(styrene sulfonic acid) and which can be sulfonated selectively. Having the sulfonic acid group in the side chain has further advantages as has been described in the literature e.g. by Lafitte et al. or Li et al.[12–14]

Secondly an alternative synthetic route has been evaluated in this work namely the preparation of poly(ether sulfone)s by a melt polycondensation process, firstly described by Kricheldorf et al.[15,16]

Experimental Part

Materials

4,4′-difluorodiphenylsulfone (DFDPhS) was purchased from Aldrich and was used as received. 2,5-dihydroxybiphenyl (phenylhydroquinone; PhHQ) was purchased from Acros. Hexamethyl disilazane (HMDS), 4,4′-dihydroxydiphenylsulfone (DHDPhS) was a product of ABCR. Toluene, dichloromethane and N-methyl-2-pyrrolidone (NMP) were all obtained from Merck. Cesium fluoride and trifluoroacetic acid were purchased from Aldrich.

Silylation of Bisphenols

0.5 mol of the respective bisphenol was refluxed in a mixture of 0.5 l toluene and 0.6 mol of HMDS. After the evolution of ammonia had ceased, toluene and excess HMDS were removed under reduced pressure. The purified products were finally obtained in quantitative yield by vacuum distillation (Table 1).

Polymerization

The poly(ether sulfone)s were obtained by the reaction of 4,4′-difluoro diphenylsulfone with the trimethylsilylethers of 4,4′-dihydroxydiphenylsulfone and 2,5-dihydroxybiphenyl in various compositions in the melt as described elsewhere.[18]

Poly(ether ether ketone)s were obtained by nucleophilic displacemant reaction carried out in solution.

The compositions and molecular weights of samples prepared in this work are summarized in Table 2.

Sulfonation

The sulfonation was carried out at elevated temperature in a solution of the respective

Table 2.
Composition and basic polymer properties of poly(ether sulfone)s.

Sample	PhHQ	DHDPhS	η_{inh} (dl/g)[a)]	M_w[b)]	M_n[b)]	DP	Tg (°C)
PES-0	0	1	0.37	44000	20000	2.2	228
PES-I	1	3	0.63	111000	48000	2.3	229
PES-II	3	5	0.44	67000	29000	2.3	217
PES-III	1	1	0.43	72000	35000	2.1	210
PES-IV	5	3	0.39	58000	24000	2.3	206
PES-V	3	1	0.41	71000	30000	2.4	199
PES-VI	1	0	1.17	230000	81000	2.8	191

a) c = 2 g/l in DMAc at 30 °C;
b) From GPC measurements; eluent DMAc containing 2 vol.-% water and 3 g/l LiCl, poly(vinylpyrrolidone) standards were used for molecular weight calibration.

polymer in CH_2Cl_2/TFA or chloroform using either conc. sulfuric acid or chlorosulfonic acid trimethylsilylester.

Measurements

The viscosities were measured in dimethyl acetamide (DMAc) with c = 2 g/l using an automated Ubbelohde viscosimeter thermostated at 25 °C.

DSC measurements were carried out with a Netzsch DSC Phönix 408 at a heating rate of 20 K/min. The second heating scan was used to determine the T_g.

^{1}H spectra were recorded on a Bruker AMX 500 spectrometer operating at 500.13 MHz for ^{1}H. DMSO-d_6 served as the solvent and internal chemical shift reference (2.5 ppm for ^{1}H).

Molecular weights were obtained from GPC measurements on a Knauer GPC equipped with two Zorbax PSM Trimodal S columns and a RI detector. A mixture of DMAc with 2 vol.-% H_2O and 3 g/l LiCl was used as eluent. Polyvinylpyrrolidone samples served as standards for molecular weight calibration.

The water-uptake was measured by soaking a piece of dry membrane in water for 24 h at 25 °C. The excess water is wiped off gently with a tissue and the sample is weighed immediately. Subsequently, the membranes were dried at 80 °C in vacuum to constant weight. The water-uptake is calculated using equation (1) and is given in percentage increase in weight, where m_{wet} and m_{dry} are the weights of the water-swollen and dry membrane sample, respectively.

$$W = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\% \qquad (1)$$

The ion-exchange capacity (IEC, with units mmol/g of dry polymer) of the sulfonated membranes was measured using the standard experimental method of immersing the membrane in 1N HCl for 24 h, followed by soaking in distilled water to remove excess acid for another 24 h. Finally, the membrane samples are soaked for 1 day in 2 M NaCl solution (exchange of H^+ by Na^+ within the film) and then titrating the solution with 0.01N NaOH to determine the concentration of the exchanged protons.

Results and Discussion

Poly(ether sulfone)s of high molecular weight and narrow molecular weight distribution were synthesized by the so-called "silyl-method" in the melt. Molecular weights and thermal properties are summarized in Table 2. The reaction scheme is outlined in Figure 1.

Although a block-like structure of the copolymers might be deduced from the reaction course, all polymers showed a single glass transition between 190 °C and 230 °C depending on the monomer composition. The higher the PhHQ content the lower the T_g. These results suggest that the length of the possibly formed blocks are to short to induce a phase separated morphology. For a physical mixture of the two homopolymers two T_gs were found at 191 °C and 222 °C, indicating a phase separation between the two different polymers. For the sulfonated polymers no T_g could be detected.

The sulfonation was carried out in solution using two different sulfonating agents, namely conc. sulfuric acid and chlorosulfonic acid trimethylsilylester. The water-uptake at 25 °C, expressed in terms of mol water per mol sulfonic acid group increased with increasing degree of sulfonation (DS). Samples with a DS similar to Nafion 117 had a water-uptake of ca. 17 mol water per mol sulfonic acid group, which is close to that of Nafion 117 (18). The plot $IEC_{theo.}$ versus $IEC_{titr.}$, visualized in Figure 2 (closed symbols), from samples sulfonated with conc. sulfuric acid shows, that some over-sulfonation occurred. This means, not only the pendant phenylring was sulfonated but the polymer main-chain as well. These findings are contrary to the results obtained with poly(ether ether ketone)s with a similar structure.[19]

NMR spectroscopic investigations revealed that the degree of sulfonation

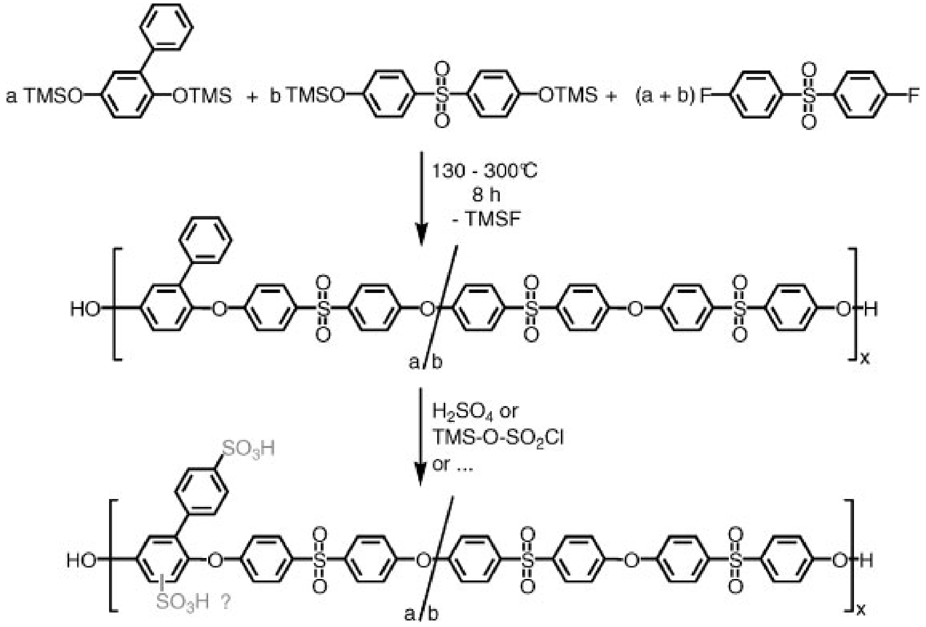

Figure 1.
Reaction scheme for the preparation of sulfonated poly(ether sulfone)s.

and the extent of main-chain sulfonation depended strongly on the sulfonating agent (Figure 3A and 3B). With sulfuric acid as sulfonating agent the sulfonation of the pendant phenylring was favored over the sulfonation of the main-chain. In case of chlorosulfonic acid trimethylsilylester, which is a milder sulfonating agent than sulfuric acid, the sulfonation occurred to 75% at the main chain. Additionally, the

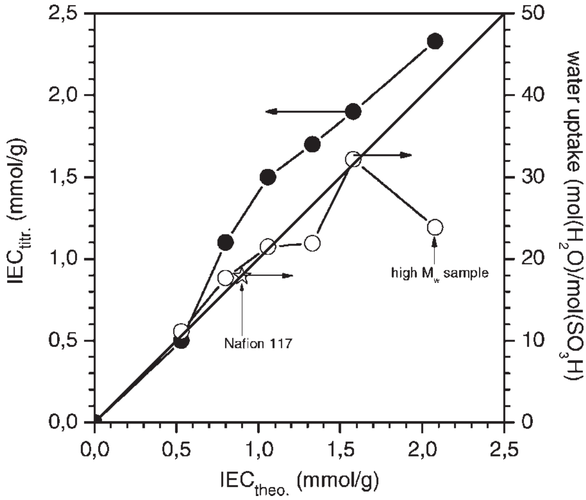

Figure 2.
Determined IEC ($IEC_{titr.}$; closed symbols) and water-uptake (open symbols) as function of theoretical IEC ($IEC_{theo.}$).

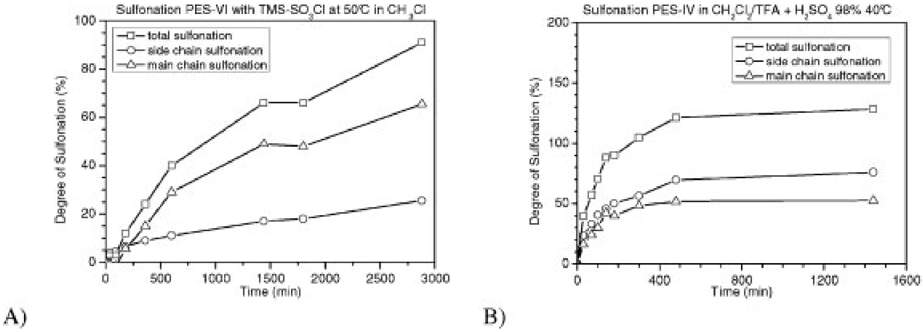

Figure 3.
Course of sulfonation of poly(ether sulfone)s with different sulfonating agents.

sulfonation with conc. sulfuric acid was much faster than with chlorosulfonic acid trimethylsilylester.

For stability tests the sulfonated polymer samples were treated in water at 130 °C for 168 h. Although some of the samples dissolved under such conditions, no hydrolytic cleavage of sulfonic acid groups nor polymer backbone degradation was detected (Figure 4).

The diffusion coefficients for methanol and protons in sulfonated poly(ether sulfone) membranes together with the values for a Nafion membrane are displayed in Figure 5 as a function of water-uptake. The procedures for the measurement and the calculation of the diffusion coefficients were adopted from the literature.[20] As expected, the diffusion coefficients for both methanol and protons are increasing with

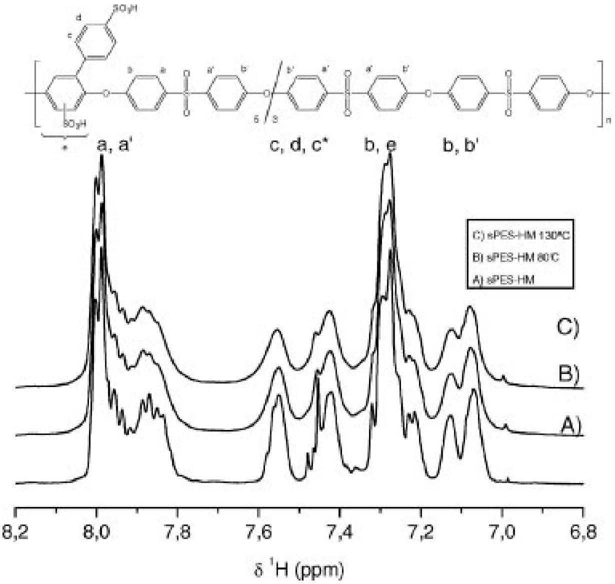

Figure 4.
NMR spectra of sPES-IV before thermal treatment (A) and after thermal treatment for 168 h at 80 °C (B) and 130 °C (C), respectively.

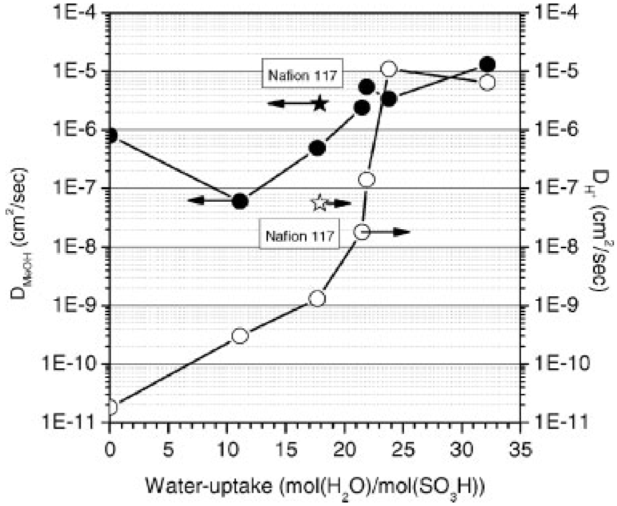

Figure 5.
Transport properties of sulfonated poly(arylene ether sulfone) membranes compared with Nafion 117 at 25 °C.

increasing water-uptake (IEC), due to higher hydrophilicity and an enhanced swelling of the membranes (Figure 2). While the methanol diffusion coefficient increases moderately with ''bound'' water in the membrane (IEC), the proton diffusion coefficient shows a steep increase of four orders of magnitude in the range of 17 to 25 mol water per mol of sulfonic acid group. In this range of bound water the methanol diffusion coefficient is comparable to that of Nafion 117 while the proton diffusion coefficient is up to two magnitudes of order higher.

Conclusions

The silyl-method has been successfully applied for the synthesis of high molecular weight poly(ether sulfone)s from *O,O′*-bis-trimethylsilyl-phenylhydroquinone, bis-trimethylsiyl-(4-hydroxy phenyl)sulfone and bis(4-fluoro phenyl)sulfone. This special method avoids large amounts of solvent and catalyst during the synthesis step. Contrary to the findings from the sulfonation of similar PEEK, the post-sulfonation of PES samples with sulfuric acid or chlorosulfonic acid trimethylsilylester leads to an undesired double sulfonation of the phenylhydroquinone moieties in the polymer backbone. Despite that over-sulfonation, samples with an IEC up to 1.50 mmol/g (water-uptake of 25 mol water/mol sulfonic acid group) showed promising properties concerning future application e.g. as ion-exchange membranes in fuel cells.

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